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THE COKING OF COAL AT LOW TEMPERATURES WITH SPECIAL REFERENCE TO THE PROPERTIES AND COMPOSITION OF THE PRODUCTS

BY

HUBERT LEONARD OLIN
B. A. University of Iowa, 1908
M. S. University of Illinois, 1911

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H. L. OLIN

CONTENTS

		PAGE
I.	Introduction	3
	1. Preliminary	3
	2. Resumé of Previous Work	3
	3. Outline of Present Investigation	4
II.	Experimental Work	4
	4. Description of Coking Oven	4
	5. Coking Tests	6
	6. Gas Producer Tests	11
	7. Adaptation of the Coke to Domestic Appliances	18
	8. The Sources and Uses of Coal Tar	18
	9. Methods for Testing and Analyzing Tars	19
	10. Properties of Tar Products From Low Temperature Coal Distillation	20
	11. Distillation of Tar	21
	12. Examination of Light Oil	22
	13. Examination of Heavy Oil Fraction	25
	14. Pitch	26
	15. Oxygen Absorbing Power of Tar	27
III.	Appendix of Supplementary Results	27
IV.	Summary	29
V.	Review of Literature	30

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To Professor S. W. Parr, in whose laboratory the author has spent the three years of his graduate work and under whose direction the work was done, he owes a special debt. Professor Parr's qualities of thorough scholarship combined with rare tact and human kindness have made the association doubly profitable and pleasant.

THE COKING OF COAL AT LOW TEMPERATURES WITH SPECIAL REFERENCE TO THE PROPERTIES AND COMPOSITION OF THE PRODUCTS

I. Introduction.

1. *Preliminary.*—This report covers a series of studies made during the period from 1911 to 1913 on the coking properties of Illinois coal. It is a continuation of the work described in Bulletin No. 60 of the University of Illinois Engineering Experiment Station.* Its distinctive feature has been the use of an apparatus which would yield the main products of coke, gas, and tar in quantities sufficient for a detailed study of these products, and, to a certain extent, quantities sufficient for a determination of their values by practical tests on a commercial scale.

2. *Resumé of Previous Work.*—In the experiments described in Bulletin No. 60 the apparatus used had a capacity of 6 to 8 pounds of coal at a charge. Notwithstanding this limited capacity, certain fundamental facts were developed as follows:

(a) The formation of coke depends upon the presence of certain constituents having a melting point which is lower than the temperature at which decomposition or carbonization takes place.

(b) Oxidation of these compounds may easily take place and the greatest coking effect is obtained where the opportunity for the minimum amount of oxidation has occurred. The condition prescribed, therefore, is that there shall be the least possible exposure to oxidation either before or during the process of carbonization.

(c) Coals containing an excessive quantity of the coking substance produce a light porous coke. The texture of the product may be modified by use of pressure and by close packing of the charge and

*The Coking of Coal at Low Temperatures, by S. W. Parr and H. L. Olin.

especially by mixing with material which has already passed through the coking process. Such a mixture provides the physical conditions whereby the gases formed may readily pass out of the mass without carrying along the cementing substances.

(d) By use of temperatures between 400° and 500°C. all of the resulting products are of a type distinctly different from those obtained by the usual high temperature procedure.

3. *Outline of Present Investigation.*—An apparatus was designed to utilize about 100 pounds of coal. Experience in the use of the apparatus indicated also the main principles which should be embodied in a commercial equipment. The coking process was studied, and the mixture for producing the best product determined. It was found that a smokeless fuel may be produced especially well adapted to domestic purposes, including its use in open grates. Its freedom from tar or condensable hydrocarbons makes it easily adapted to generating producer gas, thus affording a good substitute for anthracite coal in suction gas producer practice.

In the study of the composition and properties of the tar, this material was found to have a very low content of free carbon, a relatively high percentage of light boiling distillate, and an unusually high content of tar acids or phenols. The latter fact is of special interest to the wood preserving industry.

II. Experimental Work.

4. *Description of Coking Oven.*—The apparatus used in the experiments is an elaboration of that employed in 1910, described on page 5 of Bulletin 60, and is capable of producing material in greater quantities than was possible with the older type.

The device was manufactured by Burr and Company of Champaign, Illinois, and is illustrated in Fig. 1. As shown in the detailed diagram Fig. 2, it consists of a boiler plate shell A, lined with asbestos to prevent excessive radiation of heat; within this, forming the coking chamber, is a shell B of the same material containing a cone of light sheet iron C, perforated with 3/16 in. holes, designed to confine the coal charge and to allow a free circulation of gases. To obtain the non-oxidizing atmosphere such as was used with the old apparatus, steam was admitted from the high pressure main at E, passed through the coil F where it was superheated by the hot currents ascending from the gas burner and then conducted into the coking chamber. The heat was supplied by a blast ring burner D, connected with the gas and air

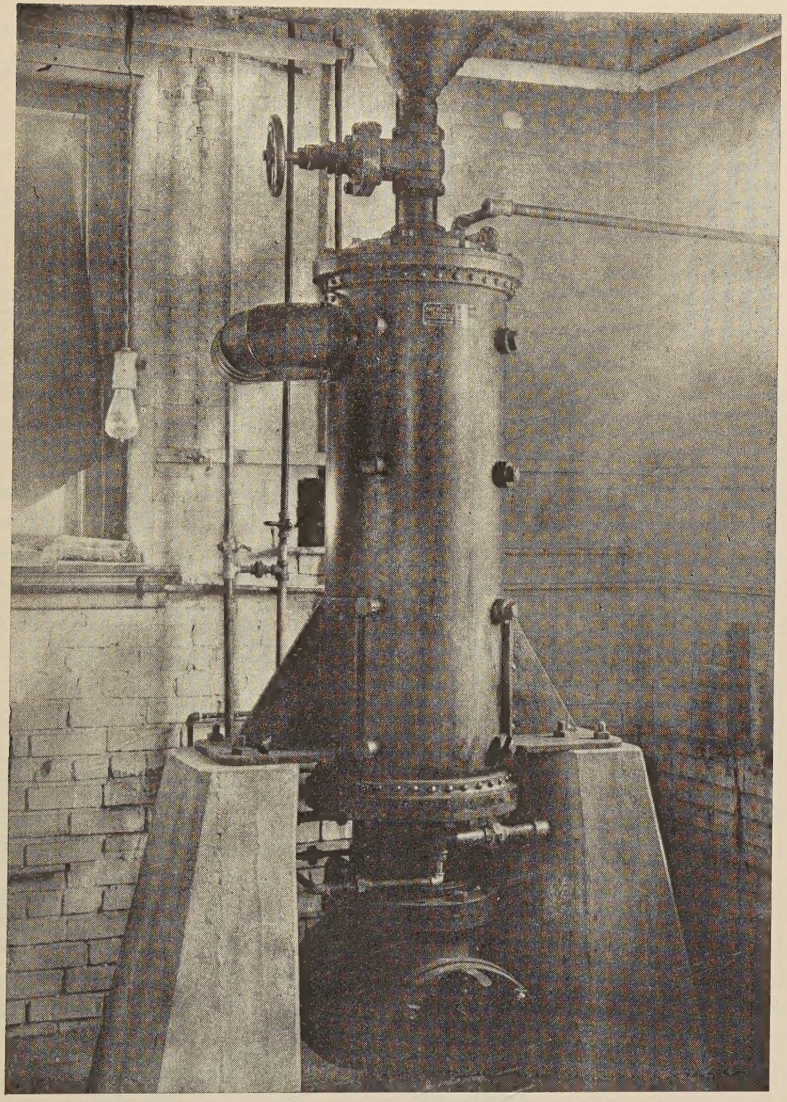

FIG. 1. APPARATUS FOR LOW TEMPERATURE DISTILLATION OF COAL

mains, and no difficulty was experienced in producing the desired temperatures. The charge of crushed coal was fed into the hopper G and admitted to the retort through a large gate valve. The coked residue was removed, after cooling the apparatus, through the bottom at H. Gases of combustion escaped through the opening J, which was connected with a flue, while the distillates were conducted through an outlet pipe to a condenser consisting of several four-foot lengths of inch pipe connected by return elbows. Cold water was allowed to drip over this gridiron-like contrivance. The tars were passed through a water sealed exit at the bottom, while the gases, fairly clean, were collected in a gasometer.

5. *Coking Tests.*—To study further the coking qualities of Illinois coals at temperatures ranging from 400°C. to 500°C. and to obtain a quantity of the coke residue sufficient in amount for practical tests in order to determine its commercial value, a series of runs was made using the apparatus described. Numerous coals from the different fields of the State were included in this set of experiments. In this report, however, products from representative types only are illustrated and described since the results of tests of different coals of a given field showed little variation. Of particular interest during the process of distillation was the behavior of the coals from the northern districts, especially those from Vermilion County. As the heating progressed, a black pitchy substance dripped from the joints of the containing ovens but it hardened immediately on cooling, forming a brittle mass much resembling asphalt. This was undoubtedly the cementing principle which is instrumental in forming coke. According to Lewes it consists of substances derived from the resins of the original coal sources, which melt at about 300°C. and decompose at slightly higher temperatures yielding on the one hand liquid products which distil out as tar vapors and hydrocarbon gases, and on the other, a pitch residuum, which at 500°C. forms a mass of coke. His general theory that these resinic substances are readily oxidizable and in their oxidized condition have much to do with coke formation is borne out in these experiments by the fact that no weathered coal of any type produced the gummy exudation mentioned, although there was no apparent diminution in the amount of gases given off. Compared with the bituminous coals of the Eastern States, those of Illinois are exceedingly rich in this resinous binding material. Even those from the southern districts of the State while not as "fat" as those from Sangamon and Vermilion Counties, nevertheless, much surpass in this respect coals like the Pocahontas, and those from Ohio and Pennsylvania. Strangely enough the abun-

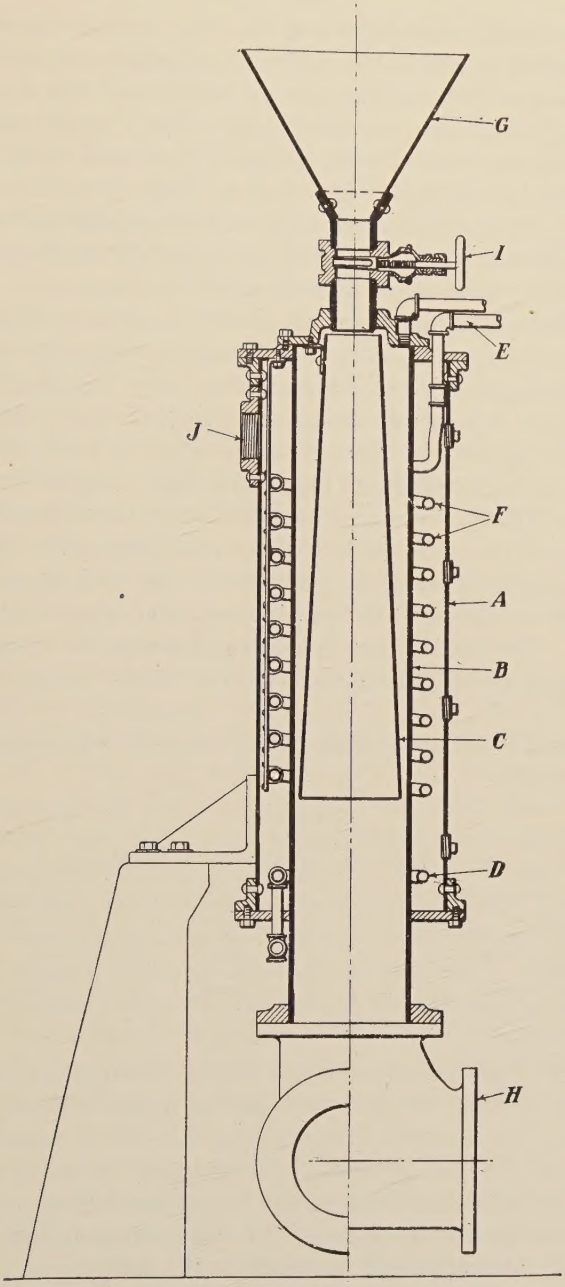

FIG. 2. CROSS SECTION OF APPARATUS FOR LOW TEMPERATURE DISTILLATION OF COAL.

dance of the coking material which the western types possess is the cause of their inferiority in the matter of making dense, hard coke; for with the decomposition of the resinic bodies and the deposition of cementing carbon there occurs at the same time an evolution of large quantities of gases which inflate the pasty mass and make the resulting coke more or less light and spongy. Indeed, certain Vermilion County coals, after being heated under conditions which allow free expansion, present the appearance of hardened froth, because of the excessive development of cell structure in the coke.

As has been shown in the previous work the porosity of the product may be appreciably reduced by subjecting the contents of the oven during the heating period to a considerable pressure. Another means to the same end which was recognized in the first experiments and which has been applied in the latter series is the addition of inert coke dust to the raw coal as fed into the retort. This material acting in the capacity of a "blotter" reduces the plasticity of the softened mass and allows the gases to escape freely without producing a blowing effect.

The diluting medium in the case of the specimens shown here was a mixture of various semi-cokes which had accumulated in the course of the work. The material was crushed and ground to a fineness of 40 or 50 mesh and thoroughly mixed with the rest of the charge in ball mills.

An analysis of a composite sample of this semi-coke breeze gave the following results:

TABLE 1.

COMPOSITION OF INERT COKE MIXTURE.

	Actual	Dry
Moisture	1.85	
Ash	11.90	12.15
Volatile Matter	19.85	20.22
Sulphur	2.62	2.67
Fixed Carbon	66.40	67.65
Calorific Value (B. t. u.)	11243	11454

The effect of the addition of this foreign substance is exceedingly interesting. Certain types of coal, as for instance those from Vermilion County, produce hard firm coke when mixed with as much as 100 per cent of their own weight of the coke dust; those from the southern districts with higher fixed carbon do not need so great a dilution. Not only is the texture made firmer by this treatment but the density is increased. Attention will be called to the differences in the properties of the cokes in discussing the individual samples.

Coke was made first from Vermilion County screenings such as were furnished the power plant of the University of Illinois. In order to remove the dust which may have been more or less weathered, the coal was passed over a quarter inch screen.

The resulting coke, shown in Fig. 3, is extremely light and porous, having a specific gravity of only .650. Its texture is firm, notwithstanding the low temperature at which it was formed and it has proved its ability to stand considerable handling without excessive dusting. Moreover, its porosity probably accounts in a large measure for the success obtained in using it in the gas producer test described later, since the carbon is easily accessible to the blasts of hot air and steam.

The coke shown in Fig. 4 was made from Saline County coal and was obtained from a run in which the time and temperature conditions were the same as in that of B-10. It illustrates the superiority of a coal from the southern field for coking purposes. Compared with the Vermilion County sample its texture is hard and firm and it has a density more than 6 per cent higher than the latter. It may be seen by referring to the photographs that the cellular structure of the Saline County sample is relatively close and solid, and bears little resemblance to the other.

One of the best products obtained in this series of experiments was from a coal from Williamson County. This sample, B-16, Fig. 5, shows a fine even grain and has a density of .750, more than 15 per cent higher than B-10. It has remarkable strength, both tensile and compressive, and stands rough handling without appreciable dusting.

Other coals from Williamson County have shown the good coking qualities which characterize the southern types. The particular sample illustrated in Fig. 6 shows an uncarbonized center but the outer portion is consistently dense and hard and has considerable strength.

In the course of the work tests were made of many coals from other localities as well as from different beds in the same locality. Included in the list are samples from Perry, Franklin, Jefferson, and Jackson Counties, but the cokes made from them are so similar in quality to those already described that they are not separately discussed.

TABLE 2.

COMPOSITION OF COKE FROM RAW COALS.

Sample	Moisture	Ash	Volatile Matter	Fixed Carbon	S	Heat Value B. t. u.
B-10	1.85	13.8	13.20	71.10	3.0	11891
B-12	1.20	11.9	10.85	75.95	1.6	12520
B-16	3.25	12.4	11.50	72.85	1.5	12600
B-19	2.25	11.75	12.30	73.70	1.55	12415

The effect of the addition of a fine inert diluting medium to different types of raw coal is seen in samples B-18 and B-21, Fig. 7 and Fig. 8. The former is the product from the heating of a mixture of equal parts of Williamson County coal and the coke dust described on page 8. It is loose in texture and crumbles easily showing a deficiency in bonding material. On the other hand, B-21, made from equal parts of Vermilion County coal and the coke in question, is quite as hard and firm as the raw coal product and considerably denser. B-22, Fig. 9, is from Vermilion County coal diluted with one-half its weight of inert material and while it resembles B-21 it has a lower specific gravity.

Williamson County coal although unable to cement itself firmly when mixed with an equal weight of non-coking material nevertheless works successfully in a mixture of two parts coal to one part inert material. B-25, Fig. 10, is both coherent and dense proving that the dilution limit has at least not been exceeded in applying this mixing ratio.

Saline County coal likewise produces better coke with the addition of foreign material. B-13, Fig. 11, raw Saline County coal two parts and coke dust one part, is superior in every way to the coke from the raw coal alone.

The composition of this series of samples is given in the following table.

TABLE 3.

COMPOSITION OF COKES FROM MIXTURES OF COAL AND COKE DUST.

Sample	Moisture	Ash	Volatile Matter	Fixed Carbon	S	Heat Value B. t u.
B-21	1.35	14.95	13.7	70.0	3.15	11750
B-18	1.30	12.9	13.90	71.90	2.50	12295
B-22	1.60	14.50	12.70	71.20	2.9	11825
B-13	1.40	14.2	15.22	69.18	2.8	12150
B-25	1.45	15.4	10.50	72.65	3.0	11920

The rise in the density of the coke with the addition of the inert substance is shown by the results of the following specific gravity measurements.

TABLE 4.

DENSITIES OF COKES.

Description		Density
Saline County Coal	B-12 (unmixed)	.687
	B-24 (raw ¾, dust ¼)	.775
	B-13 (raw ⅔, dust ⅓)	.868
Williamson County Coal	B-16 (unmixed)	.750
	B-25 (raw ⅔, dust ⅓)	.969
Vermilion County Coal	B-10 (unmixed)	.650
	B-22 (raw ⅔, dust ⅓)	.848
	B-21 (raw ½, dust ½)	852

For purposes of comparison it is interesting to note that B-29, Fig. 12, a 16-hour Solvay coke from an Illinois coal has a density of .830; B-30, Fig. 13, a 48-hour compressed charge, .986; while a representative sample of bee-hive Connellsville has a density of about 1.12.

While the methods described in the foregoing may not be applied directly on a commercial scale to operations for making metallurgical coke, still it is hoped that the results obtained may at least help to establish the characteristics of the coals of the State with regard to their adaptability to this use and to suggest methods and principles on which to work in solving the problem of making cokes of good quality from such material. Unquestionably they possess coking properties to a marked degree but need to be treated differently from the eastern coals with their higher percentages of fixed carbon.

6. *Gas Producer Tests.*—Early in the course of this work, the study of the products resulting from the distillation of bituminous coals at low temperatures suggested the possibility of using them as fuels for the gas producer whereby it was hoped to obtain gases sufficiently free from tar to be suitable for use in the internal combustion engine. Previous experiments had shown that the moderate temperatures of the preliminary heating period were effective in expelling the major part of the tar-producing substances and that the residue, distilled a second time at high temperatures, yielded gases remarkably free from heavy condensation products.

In order to give the matter a practical test, arrangements were made with Professor C. R. Richards of the Department of Mechanical Engineering of the University of Illinois for the use of the necessary apparatus of his department and with Mr. A. P. Kratz of the Engineering Experiment Station for his services in conducting the trial

run. By means of the device already described a quantity of coke was prepared and it was fired in the usual manner.

The fuel used in this test was the semi-coke product obtained in subjecting Vermilion County screenings from the University power plant to low temperature distillation (400°C–550°C). This test material, four or five hundred pounds in weight, consisted of pieces varying in size from three-fourths of an inch to two inches in diameter, but the charge as fired contained some dust. It was light and porous and lay on the fuel bed without showing much tendency to pack. The following tables show its composition.

Table 5.

Proximate Analysis of Producer Test Fuel.

Moisture	2.28
Ash	15.82
Sulphur	3.13
Volatile Matter	18.00
Fixed Carbon	63.90
Calorific Value (B. t. u.)	11601

Table 6.

Ultimate Analysis of Producer Test Fuel.

Carbon	69.86
Hydrogen	2.76
Oxygen	5.15
Nitrogen (estimated)	1.00
Sulphur	3.13
Ash	15.82
Water	2.28

The producer used was a Number 3 Otto, designed to operate on anthracite pea coal, with a wet scrubber attached. The latter was merely a shell filled with coke through which the gas, admitted at the bottom, passed counter to a stream of water flowing from the top. Using anthracite coal the normal capacity of the producer was 4500 cu. ft. of gas per hour.

In place of the gas engine which under normal working conditions draws the gas from the scrubber, a Schütte-Köerting steam ejector was used. This delivered the mixture of steam and gas to a condenser and thence to a Westinghouse meter of the wet type which had been calibrated just before the test was made.

Inasmuch as the supply of fuel was limited the usual method of

starting and stopping was varied somewhat. Before beginning the experimental part of the work, the producer was fired with anthracite and thoroughly warmed up. This fire was then drawn and a new one made with a weighed amount of wood and the fuel to be tested, and the operation continued until gas of a good quality was given off, when the test was declared begun. During this preliminary period, as in the rest of the run, the measured gas was sampled by means of the continuous sampler which is a part of the installation.

At the close of the test, the fuel bed was burned as low as was deemed practicable, the ash pit cleaned, and the ash weighed and sampled. The residue on the grates was then drawn out, quenched, weighed, and sampled.

After the test was started all the coal put into the producer was weighed. The total fuel charge used in the test then included the coal equivalent of the wood and coal used to start, plus the coal fired during the test, minus the coal equivalent of the carbon in the gas given off before the formal start, minus the coal equivalent of the residue in the fuel bed at the close. Putting this into a formula:

$$W = W_1 + W_2 - \frac{(W_3 + W_5)\ 14560 + W_4 \times 62000}{H}$$

W = Total weight of equivalent coal fired during test.
W_1 = Total weight of equivalent coal in producer at start.
W_2 = Total weight of coal fired during test.
W_3 = Total weight of carbon appearing in gas before starting.
W_4 = Total weight of hydrogen appearing in gas before starting.
W_5 = Total weight of carbon within fuel bed at close of test.
H = Heating value of the coal, B. t. u.

Since the first sample contained practically no hydrogen the last term in the above formula becomes zero.

Gas samples were drawn from a point beyond the ejector where the gas was under pressure, and were taken over mercury. Coal and ash samples were taken in the usual manner.

Water fed into the vaporizer was weighed in a tank on scales. The weight of the overflow from the vaporizer was obtained in the same manner, and the weight of the water going into the fuel bed from this source was the difference between these two.

All temperatures were taken with mercury thermometers with the exception of that of the gas at the producer outlet which was obtained by means of a Hoskins pyrometer.

An attempt was made to get tar samples just as the gas left the producer but it was found that the amount of tar formed was not appreciable and the sampling was discontinued.

The Junker calorimeter was used to obtain the heating value of the gas, about one sample an hour being taken.

The form for recording the results of this test is abridged from the one given in Bulletin* No. 50 of the University of Illinois Engineering Experiment Station, where details of methods of computation may also be found.

The firing sheet for this test showed that the producer ran successfully and gave little trouble. Because of the small diameter of the fuel bed, resulting in considerable friction, the lightness of the material used, and its slight tendency to coke and arch, the fuel above the bed proper did not feed down as rapidly as it was burned. Hence it was necessary about once an hour to poke it down with a slice bar and in this respect it probably required a little more attention than a charge of anthracite.

It may be noted, however, that it was necessary to poke and clean the grates from the bottom but once during the six hours of the trial. With so small a producer this indicates a remarkable freedom from ash and clinker trouble. On cleaning the fire small pieces of clinker were found in the ash, but there was none at all sticking to the sides, where it usually collects. The high grate efficiency, 98.2 per cent, also shows that the fires required little attention, since poking and cleaning invariably force much unburned carbon out into the ash.

The fact that the fire required so little attention has an added significance in connection with a producer having a small fuel bed, such as the one used in this test. Usually, the inrush of air, when the doors are opened for cleaning, dilutes the gases sufficiently to make them too lean to burn, but with the fuel in question less trouble was experienced in this respect than is usually the case with anthracite, for at no time did the pilot flame go out and there was no great variation in the calorimeter readings.

A study of the temperature of the gas leaving the producer throws considerable light on the condition of the fuel bed. If the bed becomes clinkered, or if holes form in the fire, air goes through without coming into intimate contact with the carbon. This chimney effect causes the

*Tests of a Suction Gas Producer. Garland and Kratz. 1912.

gas to burn at the surface of the bed and the temperature to rise. Sometimes it is very difficult to keep the temperature down and cleaning and poking have little effect. In the case under discussion, however, the temperature never rose above 420°C except during the last twenty minutes of the test, when the fire was so low that it was essentially a furnace and not a producer.

No trouble was experienced with tar. There was little evidence of its presence in the fuel bed, and an attempt to get a sample of it from the gas leaving the producer showed that it was present in negligible quantities only. On cleaning the ejector at the close of the run a small amount of tar was noticed but most of the deposit was of the nature of scale. It is to be remembered that before going to the ejector the gas had first passed through the scrubber.

The efficiencies (hot gas 74.4 per cent and cold gas 64.9 per cent) compare very favorably with those obtained in using anthracite coal of the same ash content.

Data and results are given in the following table.

TABLE 7.

RESULTS OF GAS PRODUCER TRIAL.

Made by A. P. Kratz and H. L. Olin.	
Mechanical Engineering Laboratory, University of Illinois.	
Make of Producer, Otto.	
Kind of Fuel—Semi-coked Vermilion County Coal.	
Type of Producer—Suction for Anthracite.	
Duration of Trial—hours	6.33
DIMENSIONS AND PROPORTIONS	
Great area, sq. ft.	1.666
Mean diameter of fuel bed, ft.	1.545
Depth of fuel bed, ft.	2.21
Area of fuel bed, sq. ft.	1.877
Approximate width of air spaces in grate, inches	0.5
Area of air space, sq. ft.	0.722
Ratio of air space to whole grate	0.433
Area of discharge pipe, sq. ft.	0.165
Water heating surface in vaporizer, sq. ft.	2.7
AVERAGE PRESSURES	
Average corrected barometer reading, inches mercury	29.52
Draft in ash pit, inches water	0.45
Suction at producer outlet, inches water	0.88
Pressure at meters, inches water	3.69
Absolute pressure at meters, inches mercury	29.69
Vapor pressure at meters, inches mercury	1.9
Dry gas pressure at meters, inches water	27.79

TABLE 7. (CONTINUED)

AVERAGE TEMPERATURES (Degrees Centigrade)

At barometer,	28.3
Of fire room,	33.3
Of feed water entering vaporizer,	23.4
Overflow from vaporizer,	84.8
Of water entering scrubber,	14.8
Of water leaving scrubber,	45.7
Of gases leaving producer	378.0
Of gases leaving first scrubber,	34.5
Of gases entering meters,	38.2
Of gases entering meters, (absolute)	311.2

FUEL

Weight of wood used in starting, lb.	9
Volume of gas given off before start of test, cu. ft.	2238
Volume of standard gas given off before start of test, cu. ft.	2010
Weight of equivalent coal as fired, lb.	381
Percentage of moisture in coal	2.28
Total weight of dry coal fired, lb.	372
Total ash and refuse, lb.	37
Total weight of residual, lb.	49
Total weight of combustible, lb.	280.6

COMPOSITION OF PRODUCER FUEL

Fixed carbon, per cent	70.77
Volatile matter, per cent	18.00
Moisture, per cent	2.28
Ash, per cent	15.82
Sulphur, separately determined, per cent	3.13

ULTIMATE COMPOSITION OF PRODUCER FUEL

Carbon, per cent	71.50
Hydrogen, per cent	2.82
Oxygen, per cent	5.26
Nitrogen, per cent	1.02
Sulphur, per cent	3.20
Ash, per cent	16.20
Moisture in sample coal as received, per cent	2.28

COMPOSITION OF DRY ASH AND REFUSE

Carbon, per cent	14.48
Earthy matter, per cent	85.52

COMPOSITION OF RESIDUAL FUEL ON GRATE

Carbon	36.46
Volatile matter	7.10
Moisture	1.18
Ash	55.30

FUEL CONSUMPTION PER HOUR

Dry coal per hour, lb.	58.8
Dry coal per sq. ft. of grate area per hr., lb.	35.3
Dry coal per sq. ft. of fuel bed per hr., lb.	31.3

TABLE 7. (CONTINUED)

CALORIFIC VALUE OF FUEL

Calorific value by oxygen calorimeter, per lb. dry coal, B. t. u.	11601

WATER

Total weight fed to vaporizer, lb.	440.0
Total weight of overflow, lb.	256.0
Water actually evaporated in vaporizer, lb.	184.0
Weight of water fed to producer, lb.	
(a) From vaporizer	184.0
(b) In air (estimated)	6.0
(c) In coal	8.7
Total	199
Total weight of water decomposed as used in calculations, lb.	91.
Total weight of moisture in gas leaving producer, lb.	108.
Weight of water decomposed per lb. of gas generated, lb.	0.0588
Weight of water decomposed per lb. of dry coal fired, lb.	2.42
Total weight of scrubber water, lb.	5880

GAS

Calorific value per cu. ft. of standard gas from calorimeter, B. t. u. (high value)	121
Specific weight of standard gas, lb. per cu. ft.	0.0670
Specific heat of dry gas leaving producer (estimated)	0.260
Total volume of gas from meters, cu. ft.	26927
Total volume of standard gas at 16.5°C. and 30 in., cu. ft.	23150
Volume of standard gas per hr. cu. ft.	3660
Volume of standard gas per lb. of dry coal cu. ft.	62.3
Total weight of standard gas, lb.	1552.
Weight of standard gas per lb. of dry coal, lb.	4.17

COMPOSITION OF GAS BY VOLUME

Carbon dioxide, CO_2	4.15
Carbon monoxide, CO	21.10
Oxygen, O_2	0.30
Hydrogen, H_2 (estimated from calorific value)	11.80
Marsh gas, CH_4	1.50
Nitrogen, N_2 by difference	61.00

COMPOSITION OF GAS BY WEIGHT

Carbon dioxide, CO_2	7.19
Carbon monoxide, CO	23.17
Oxygen, O_2	0.38
Hydrogen, H_2	0.93
Marsh gas, CH_4	0.96
Nitrogen, N_2 by difference	67.37

EFFICIENCY

Grate efficiency, per cent	98.2
Hot gas efficiency, based on high heating value, per cent	74.4
Cold gas efficiency, based on low heating value, per cent	64.9

7. *Adaptation of the Coke to Domestic Appliances.*—A limited amount of the coke was available for testing its adaptability to house-heating purposes. The ordinary household appliance is especially well adapted for distilling off the hydrocarbons of coal and sending them into the air unburned or partly burned and accompanied by large volumes of smoke.

In the coke product here described the heavy hydrocarbons have been removed. The coke itself, therefore, is clean both in handling and in burning. However, there remains approximately 20 per cent of volatile matter which enters into the process of combustion after the coke has attained a temperature at or beyond the point to which it had been subjected in the coking process. These conditions result in a free burning substance yet one whose combustible constituents may not produce smoke in burning.

An open grate was selected as furnishing the best opportunity for observing the behavior of the material. The results are summed up as follows: the coke ignites readily, it retains its shape through the process of combustion, a bed of glowing coals quickly results, the very indifferent provision for draft as found in an open grate is sufficient for keeping the combustion lively, there is no smoke produced, and fire is retained over a long period of time, because the interior of the larger pieces holds the fire and continues the combustion until all of the carbonaceous matter is consumed. While the temperature commonly attained by a grate fire would not furnish positive evidence as to the formation of clinker, the indications so far as they went, were altogether favorable. A small amount of coke was tested by burning in a hot air furnace. Not enough material was at hand for a complete test, but so far as observations could be made, it was as favorable as the test in the open grate.

8. *The Sources and Uses of Coal Tar.*—The installation of the first American by-product recovery coke plant in 1893 marks the beginning of a notable rise in the production and use of coal tar in this country.

Previous to that time the isolated illuminating-gas plant was the only source of supply and, indeed, in the smaller places at least, the tar was looked upon as a troublesome waste product rather than as a thing of value.

For making metallurgical coke, types of beehive ovens of varying degrees of efficiency were employed and these, of course, allowed the volatile constituents of the coal, both gaseous and liquid, to be wasted.

In 1912, not twenty years after the introduction of the new type of oven, 165,000,000 gallons of tar were produced in the United States, and two thirds of this quantity, according to Perry,* came from the by-product coke plant. With the steady increase in by-product oven construction the tar refining industry will assume a proportionate importance.

Of the various fractions obtained in distilling the crude tar the most important are;—benzol and its homologues, used in the color industry and as paint and fat solvents; the carbolic oils, much in demand for disinfectants of various kinds; and the creosote and anthracene oils, of great importance in the preserving of wood. The pitch residue is used in roofing, paving, and road-building, but in these fields it meets strong competition with the mineral bitumens and consequently does not find so ready a market as the other constituents named. But pitch makes up the greatest part of the crude tar aggregate, being in most cases considerably more than half. The bulk of the raw material therefore, is in the form of high temperature condensation products and free carbon of relatively small value, while the supply of the lighter fractions is insufficient to meet the demand. This is especially true of those compounds of the tar which have bactericidal properties. With the rapid depletion of the forests and the cutting off of lumber supplies, wood preserving treatment has become imperative in many industries—particularly that of the railroads—and the lack of available material for this process is causing much concern. American supplies are inadequate for home consumption and nearly 45,000,000 gallons of creosote oils were imported from Europe in 1911. Any modification of the coking process, therefore, that will increase the yield of the light tars by preventing their condensation to compounds of high molecular weight will effect a considerable economy. Considerations of this kind have lent interest to the study of the tars obtained in the course of these experiments, in which temperatures were kept much below those of the gas retort and the commercial coke oven.

9. *Methods for Testing and Analyzing Tars.*—Of the methods proposed and outlined for testing tar, perhaps the best are those published by S. R. Church in a paper on "Methods for Testing Coal Tar and Refined Tars, Oils and Pitches Derived Therefrom."† These tests, as

*Eighth Int. Cong. of App. Chem., 10, 233.

†The Gas Age, 32, 103. Jour. of Ind. and Eng. Chem., 3, 227.

he says in the introduction, were not put forward as methods for the scientific examination of, or research into, the products of coal tar, but rather as an attempt, in cooperation with other chemists of the company with which he was connected, to revise and standardize the everyday tests applied to the raw materials and products of the American tar distiller.

In this article he takes up the determination of water, free carbon, fixed carbon, and ash, and the measuring of the specific gravity and viscosity of the raw tar, distilled tars, and pitch. He then outlines the chemical investigation of the light oils, carbolic oils, benzols and creosotes, including the estimation of napthalene. In a later paper[1] he gives some supplementary methods.

Prevost Hubbard's "Methods for the Examination of Bituminous Road Materials"[2] approaches the matter solely from the standpoint of the road-builder, and takes up the physical tests necessary to determine the fitness of the material for this special purpose. In its field it is, unquestionably, authoritative.

Among the publications devoted particularly to methods for testing wood preservatives may be mentioned those of the American Railway Engineering Association,[3] the National Electric Light Association,[4] and the Forest Service of the Department of Agriculture.[5]

In addition to the foregoing, the following works take up to a greater or less extent the subject of coal tar analysis:

Sadtler, Industrial Organic Chemistry, 3rd. ed. J. B. Lippincott Co.

Rogers and Aubert, Industrial Chemistry, 1913, Van Nostrand Co.

Lunge, Coal Tar and Ammonia, 4th ed. 1909. Van Nostrand Co.

Allen, Commercial Organic Analysis. Vol. II, part 2, 3rd. ed. 1909. Blakiston's Son and Co., Philadelphia.

Mulliken, Identification of Pure Organic Compounds. 1904. Wiley and Sons.

10. *Properties of Tar Products From Low Temperature Coal Distillation.*—The tar used in this investigation was the product obtained in a separate series of runs made with Vermilion County coal.

[1]Jour. of Ind. and Eng. Chem., 5, 195.
[2]U. S. Dept. of Agriculture, Office of Public Roads, Bulletin 38, 1911.
[3]Bulletin 65, American Railway Eng. Assoc.
[4]Report of Committee on Preservative Treatment of Poles and Crossarms, 1911.
[5]Dean and Bateman, Circular 112, "Analysis and Grading of Creosotes."

FIG. 3. B-10. VERMILION COUNTY COKE

FIG. 4. B-12. SALINE COUNTY COKE

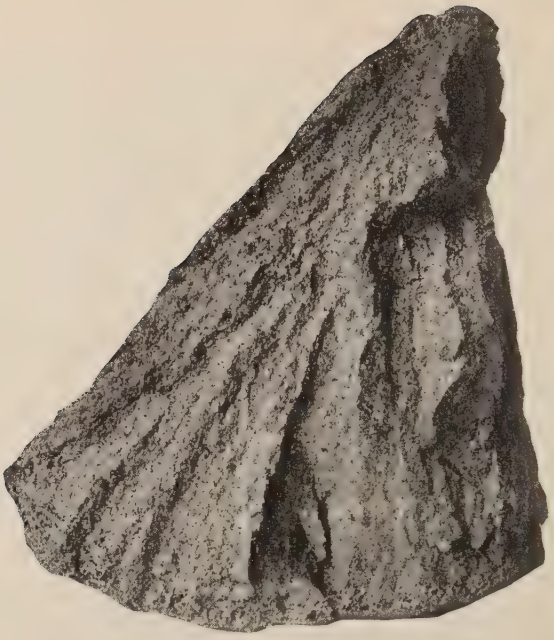

Fig. 5. B-16. Williamson County Coke

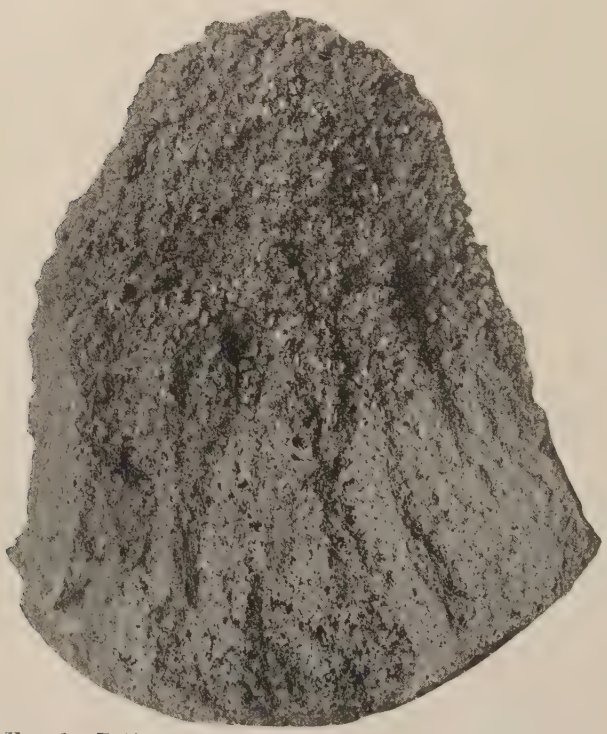

Fig. 6. B-19. Williamson County Washed Nut Coke

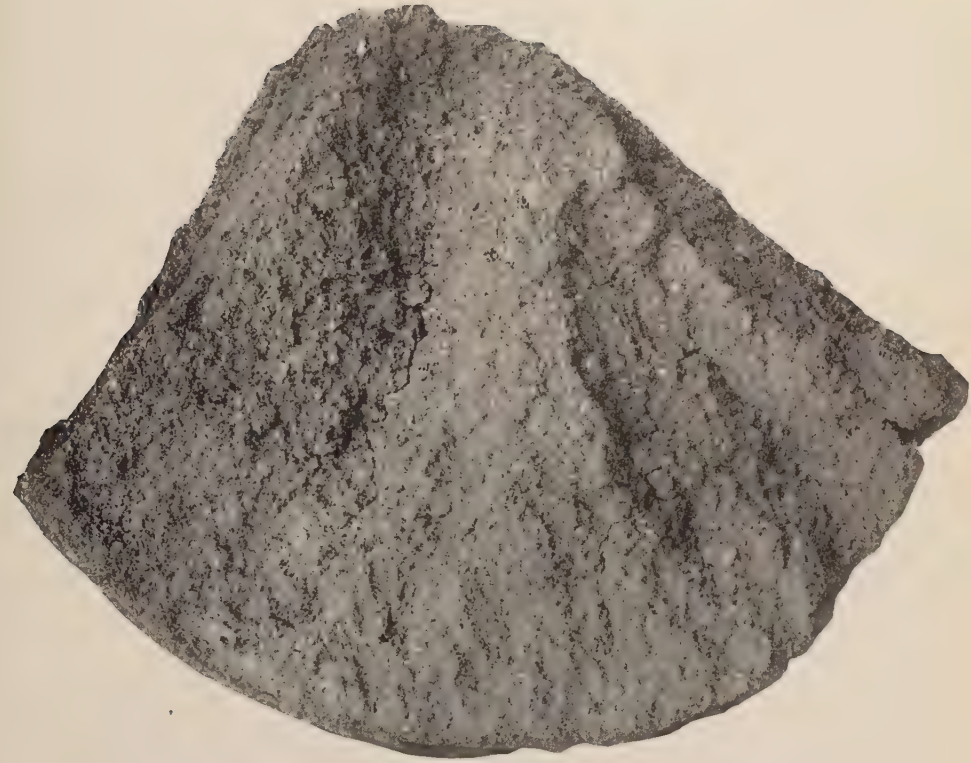

Fig. 7. B-18. Coke from Williamson County Coal Mixed with Coke Dust

Fig. 8. B-21. Coke From Equal Parts of Vermilion County Coal and Coke Dust

FIG. 9. B-22. COKE FROM VERMILION COUNTY COAL AND COKE DUST

Fig. 10. B-25. Coke From Williamson County Coal and Coke Dust

Fig. 11. B-13. Coke From Saline County Coal and Coke Dust

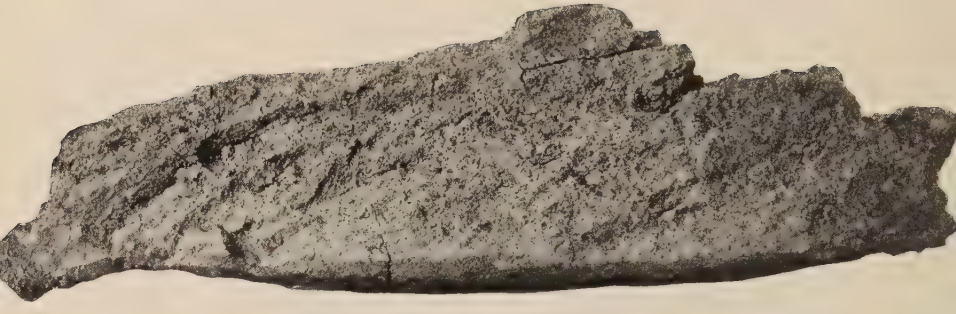

FIG. 12. B-29. 16-HOUR SOLVAY COKE

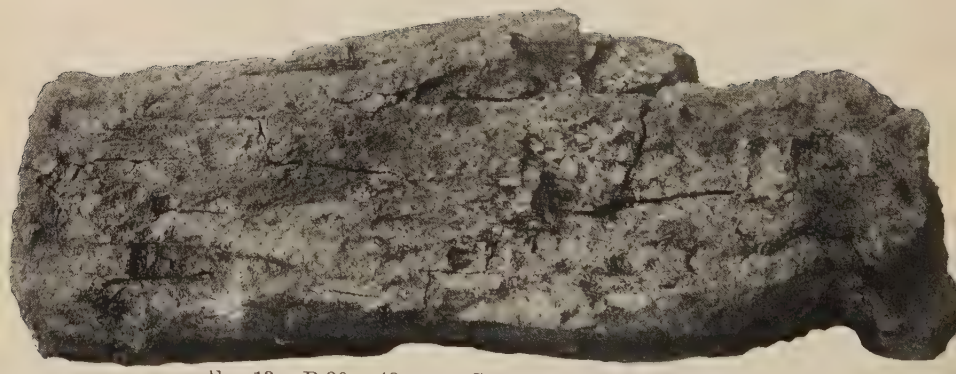

FIG 13. B-30. 48-HOUR COMPRESSED SOLVAY COKE

To prevent oxidation and evaporation the tar was protected as soon as formed with a water seal, and kept in air-tight cans until used for analysis.

The tar is fluid at temperatures considerably below room conditions. In appearance it is black to rich brown with varying thickness of layer, and it possesses an exceedingly disagreeable odor even when judged by coal tar standards.

The specific gravity measured with a pyknometer at 20° was 1.069. Its low density makes its separation from water by gravity somewhat difficult and there is a tendency, moreover, for high fractions to float on the surface of the water. Its viscosity is low and in this respect it resembles a mineral oil rather than a high temperature coal tar.

The percentage of free carbon, or more accurately, of substances insoluble in toluene and benzene, was found by treating a comparatively large sample of the dry tar, (about 36 grams) with toluene, and heating the mixture on the steam bath. The solution was decanted through two S and S filter cones (33 mm. and 26 mm.) one within the other. After three treatments the whole mass was transferred to the cones and extracted with benzene in a Soxhlet apparatus until the filtrate was colorless. Check results showed a free carbon content of 1.35 per cent.

Fixed or combined carbon may be determined by a method based on the report of the Committee on Coal Analysis of the American Chemical Society.* The cracking of an oil or tar is, however, so closely dependent upon time, temperature, and pressure conditions that a simple laboratory test of the kind outlined by the Society would have little significance.

11. *Distillation of Tar.*—In order to dry the tar a preliminary distillation 125° was made and the light oil runnings after being separated from the water were returned to the retort. The apparatus used was an ordinary Jena distilling flask attached to a Liebig condenser.

In the earlier attempts to make this separation much trouble was caused by the tendency of the water in the crude material to produce a succession of "bumpings." These explosions were often so sudden and violent as to throw a considerable part of the charge out of the retort. This annoying feature was prevented, however, by running a slow stream of air through a tube extending nearly to the bottom of the vessel, and later, in order to prevent oxidation which seemed

*Jour. Am. Chem. Soc., 21, 1116.

to take place at the higher temperatures under these conditions, carbon dioxide, which had been previously washed and dried, was substituted. This method was used in all subsequent distillations of the crude, wet tar and served the double purpose of providing an inert atmosphere in which to carry on the heating of the substances making up the material, many of which show remarkable chemical activity, and of making the boiling proceed smoothly and quietly. It is to be noted, however, that the current of gas sent through the apparatus carries over with it a considerable quantity of material whose boiling point is at a temperature above that maintained in the retort. In redistilling the dry tar to fractionate the sample this precautionary measure was unnecessary, and therefore was not taken.

The escape of the first light oil runnings was prevented by surrounding the receiving vessel with a freezing mixture. To condense the heavier part of the second fraction, only the inner tube of the condenser was used so that heat might be applied to facilitate the flow of the viscous fluid.

To insure greater accuracy a subsequent redistillation of the light oil fraction was made with the use of a Lebel-Henninger tube, with the thermometer so adjusted that the top of the bulb was level with the side neck. The Liebig condenser was used as before. With this apparatus it was possible to secure fractions with sharply defined boiling points, an important prerequisite to identifying individual compounds.

TABLE 8.

RESULTS OF PRELIMINARY DISTILLATION OF TAR.

Fraction	Temperature Range	Percentage
Light oil	below 210° C	17.2
Heavy oil	210°–325°	52.7
Pitch	above 325°	30.1

12. *Examination of Light Oil.*—The low boiling fraction purified as indicated above is a clear amber colored liquid with a disagreeable odor. It is very susceptible to the action of light and air and finally turns dark red even when sealed in an atmosphere of carbon dioxide.

The separation and identification of all the individual constituents of a substance like coal tar is a great task. Lunge, in his work "Coal Tar and Ammonia" has described more than two hundred distinct compounds which occur in tars of different qualities and his list is probably not complete. We are concerned in this work merely with a

few of the most important substances which are of interest because of their practical value and not with those which are of interest from the scientific standpoint only.

The phenols and other acid substances of the light oil were separated from the neutral and basic constituents by shaking the fraction in a separatory funnel with half its volume of 10 per cent caustic soda solution. After this treatment had been repeated until no further reduction in volume of the residue took place, this caustic solution was drawn off and acidified with sulphuric acid and the whole extracted with ether. The ether extract, when evaporated down, yielded crude phenol and its homologues.

The amines were removed from the oily residue after the phenol extraction by shaking it with dilute sulphuric acid, of sp. gr. 1.15, with warming. The solution was separated as before, neutralized with caustic soda, and the bases extracted with ether.

The method for separating paraffins and benzenes is based upon the familiar principle that the hydrocarbons of the paraffin series are practically inert toward sulphuric acid, while those of the aromatic series react with comparative ease, forming sulphonic acids, in which sulpho groups replace hydrogen of the benzene ring. These acids are very soluble in water and are therefore easily separated from the insoluble oily paraffin residues.

The process used was that adopted by the Forest Products Laboratory.* Ten cubic centimeters of the fraction to be tested were measured into a Babcock milk bottle. To this was added 40 cc. of 37 N sulphuric acid (made by adding the calculated amount of fuming sulphuric acid to the ordinary acid, sp. gr. 1.84) 10 cc. at a time. The mixture after being kept at 100° C for an hour was cooled and then whirled for five minutes in a Babcock separator. The volume of the unsulphonated or paraffin residue was read off directly. Equally good results are obtained, however, by pouring the mixture into a large volume of water and separating by means of the funnel.

As a step toward identifying those constituents which do not react with acids and bases, a sample of the oil from which the phenols and pyridines had been removed but which had not been sulphonated, was subjected to a second redistillation, with the measurement of the volumes going over between comparatively narrow limits of temperature.

A summary of the results obtained from the various tests and analyses follows:

*Bateman, E. Modification of the Sulphonation Test for Cresote. Forest Service, Circular 191, U. S. Dept. of Agriculture.

Table 9.

Light Oil Fraction (to 210°C).

Specific gravity .966

	Percentage on Basis of Crude Tar	Percentage on Basis of Light Oil Fraction
Light oil fraction	17.2	100.0
Phenols (and other acid substances	5.7	33.0
Amines (and other bases)	0.9	5.3
Paraffins	3.12	18.1

The results of the refractionation of the light oil from which the acids and bases had been removed are given in the following table:

Table 10.

Distribution of Neutral Substances in Light Oil.

Fraction	Percentage on Basis of Light Oil Fraction	Percentage on Basis of Crude Tar
20°–75° low boiling bodies	5.26	.25
75°–95° crude benzol (90%)	2.10	.38
95°–125° crude toluol	7.36	1.33
125°–170° crude solvent naptha	26.30	4.77
170°–200° crude heavy naptha	14.73	2.67
200°–210° crude heavy naptha	7.30	1.32

The classification as made in Table 10 is based on the outline for the examination of light oil as given by F. E. Dodge in his article on "Coal Tar and Its Distillation Products."* It is understood that this is a generalization only, and that it shows composition by classes of compounds rather than by individuals. However, since the different homologues of a class within rather close limits of the boiling point usually differ little in character, a fair idea of the composition of the mixture may be gained without further separation.

Fraction No. 1, besides some benzene, contains also pentanes and hexanes of the paraffin series, ranging in boiling point from 31° C to 64° C. No. 2 includes some of the heptanes boiling in the nineties; No. 3, according to tables complied from data† obtained by distilling known mixtures, consists of benzene and toluene, the latter predominating, while fraction No. 4 includes the xylenes boiling from 138° C to 143° C, with perhaps some mesitylene, b.p. 164°C. Likewise the part reported as phenols contains besides, one or all of the three cresols, although the close range of boiling points (190°, 201°, and 202°) made a quantitative fractionation of the crude extract impracticable.

*Industrial Chemistry. Rogers and Aubert, 1912. p. 492.

†G. E. Davis. Industrial Chemistry Rogers and Aubert. p. 499.

Finally, the rapid darkening of both the neutral and the active fractions on even short time exposures to air points to the presence of various unsaturated substances, difficult to isolate and probably of no great practical importance.

13. *Examination of Heavy Oil Fraction, 210°C to 325°C.*—The heavy oil obtained from the first distillation to which was added the residue boiling above 210°, from the redistillation of the light oil, is a thick viscous liquid of a rich brown color. After standing for a time a non-crystalline sediment is formed.

Tar acids were determined by the methods used in the examination of the light oils except that after the addition of the caustic soda it was necessary to warm the mixture in order to facilitate the separation, while the paraffin and aromatic content of substances was found by sulphonation as before. Likewise a sample from which the acid constituents had been removed was refractionated and the volumes of distillate given off between close temperature limits were noted.

The napthalene content was determined by cooling, with a freezing mixture, the heavy oil sample from which the acids had been extracted, in order to crystallize out any of this substance which might be present. The test gave zero results; the conclusion is that no napthalene was present. This result is confirmed by observations made when the original tar was distilled from the coal, for at no time did the tar condenser become clogged as it would if napthalene were going over even in small quantities, nor did the pungent odor of its vapors ever become noticeable.

The method for the quantitative assay of anthracene as given by Allen* was used for this material. The sample, dissolved in boiling glacial acetic acid, was treated with chromic acid slowly dropped through a reflux condenser to oxidize any anthracene present to anthraquinone. The results showed that the amount present was negligible.

TABLE 11.

COMPOSITION OF HEAVY OIL (210°C–325°C).

Specific gravity 1.032

Fraction	Percentage on Basis of Crude Tar	Percentage on Basis of Heavy Oil Fraction
Heavy oil fraction	52.7	100.0
Tar acids	22.2	42.13
Paraffins	6.2	32.66
Napthalene	.0	.0
Anthracene	.0	.0

*Commercial Organic Analysis. Vol. II, part 2, p. 229.

Distillation of the acid free samples gave the following results.

TABLE 12.

DISTRIBUTION OF NEUTRAL SUBSTANCES IN HEAVY OIL.

Fraction	Percentage on Basis of Crude Tar	Percentage on Basis of Heavy Oil Fraction
210° to 250°	2.87	10.3
250° to 270°	13.55	48.5
270° to pitch	11.53	41.2

In attempting to identify the various substances of the heavy oil fraction the worker finds the problem even more difficult than in the case of the light oil because the higher boiling points and molecular weights of the compounds make them more difficult to separate. A partial purification of the acid bearing extract of this part of the tar showed by the boiling points that a high percentage of creosols was present. The higher boiling members were not identified. It is possible that they are polyhydric phenols, such as Lewes mentions as being present in the tar from coalite and which he says form resinous masses difficult to investigate.

Fraction No. 2 is the neutral part of the cut in tar distilling known as creosote oils. Emmet and Reingruber* say of this class of substances that after removing basic, oxygenated, and crystallizable bodies, there remain several isomeric dimethylnapthalenes, the separation of which has proved unmanageable, and which constitute the major portion of the fraction.

14. *Pitch.*—The residuum from the original distillation of the crude tar is a hard, black substance, rather brittle, breaking with a bright fracture. As indicated by the table of its properties it is a hard pitch, as contrasted with soft pitch having a melting point of about 75° C.

TABLE 13.

PITCH FRACTION (ABOVE 325° C).

Per cent on basis of crude tar	30.1
Melting point	110° C
Specific gravity	1.27
Free carbon	12%

*Annalen 211, 365.

15. *Oxygen Absorbing Power of Tar.*—In the publication of the results of the preliminary studies of low-temperature tar,* attention was called to the fact that both the light and the heavy fractions were readily oxidizable and the question was raised whether these oils might not serve as drying bodies or paint vehicles by forming coatings or films on oxidation. In an attempt to approximate a quantitative measurement of this capacity for absorbing oxygen, a series of iodine absorption determinations was made, with rather variable results.

Further investigations of the kind have proved what was conceded as a probability at the time, that other reactions than those of simple saturation take place, chief among which is substitution with the formation of hydriodic acid. While fairly consistent results have been obtained in the supplementary work under strictly standard conditions, slight changes in the concentration of the iodine solution, in the time of digestion and particularly in the temperatures of the reacting substances so varied the values found that the method is deemed unreliable. Bromine is even more uncertain. Among the substances present in the tar from which hydrogen is easily displaced by the halogens are the phenols, the reaction taking place almost immediately even in the cold.

The only reliable criterion of its value as a paint drier is perhaps the actual test of its behavior when exposed to air. The light oil fraction forms a thin film when spread on a glass plate inclined to 45 degrees. Using good linseed oil as a standard for reference, it is found that the tar oil films are decidedly thinner, i.e., the oil flows more before thickening, and that the time of maximum drying is from two to three times that observed in the case of the linseed oil.

III. Appendix of Supplementary Results.

At the request of S. R. Church, head of the Research Department of the Barrett Manufacturing Company of New York, a small sample of the crude tar remaining after the conclusion of the work described, was sent to the New York Laboratories for examination. Mr. Church, in a communication commenting on it briefly, says, "This tar in its characteristics, resembles somewhat the Scotch blast furnace tars although it is higher in tar acid content than the Scotch tars, and apparently not quite so high in paraffin-like bodies. The most interesting feature to us is its exceptionally high content of oxygenized compounds of phenoloid character."

*Parr and Olin. Bulletin No. 60, University of Illinois Eng. Exp. Sta. p. 13.

"Should tar of this nature become a commercial product, it would undoubtedly have a certain value to the tar distillers although it would, of course, have to be handled in an entirely different manner from the ordinary coal tars."

The outline of his results is given in the following table.

TABLE 14.

TESTS OF TAR DERIVED FROM THE DISTILLATION OF COAL FROM VERMILION CO., ILLINOIS. (S. R. CHURCH.)

Water, per cent	21.7
Tests on Dry Tar:	
Specific gravity at 15.5°C	1.072
Free carbon, per cent	1.3
Light Oil (to 210°) per cent by vol.	15.2
Heavy Oil (to pitch) per cent by vol.	40.2
Light Oil:	
Tar acids, per cent	30.0
Sulphonation residue, per cent	15.0
Heavy Oil:	
Standard retort distillation:	
Total per cent to 170°C	0.5
200°	2.0
210°	6.6
235°	33.6
270°	61.0
315°	65.8
355°	94.9
Tar acids in total distillation	50.0
Sulphonation residues on fractions	4 to 5 per cent
Pitch	
Melting point,	76°C
Free carbon, per cent	9.0

Of equal interest is the supplementary report furnished by Mr. E. B. Fulks of the American Creosoting Company of Louisville, Kentucky, who visited the laboratory early in the year 1913 and obtained a sample of a tar similar to the one that has been discussed. He writes: "This tar is quite different from ordinary coal tar, in that it is thinner, has a lower specific gravity and much smaller percentage of pitch. The principal difference however, is in the high percentage of tar acids and in the presence of considerable quantities of paraffinoid bodies. These differences probably would make it necessary to work this tar somewhat differently from the method employed for ordinary tars but undoubtedly it would have considerable commercial value."

"The quantity at our disposal was so small that we were unable to separate an amount large enough to test the preservative qualities of that proportion which would be used for this purpose. Apparently, however, this tar would produce from 30 to 40 per cent of oil of fair preservative value. The high percentage of tar acids would make it a

valuable source of material for the manufacture of antiseptic solutions, sheep dip, etc. The pitch contains a small proportion of free carbon and probably could be used for roofing purposes and paving filler."

The report of his analysis is given in the following table:

TABLE 15.

OIL FROM LOW TEMPERATURE COKING EXPERIMENTS
UNIVERSITY OF ILLINOIS.

Description: Thick, dark brown oil, having a very disagreeable odor resembling Pintsch gas; liquid at ordinary temperature.

Specific gravity at 38° C.			1.041
Water			Trace
Tar acids by volume			27.0%
Fractions			
210°		10.6%	Liquid
235°		8.9%	"
270°		12.5%	"
315°		13.1%	"
355°		14.1%	"
Res.		40.4	
Hard, black, brittle, bright fracture.			

Paraffin Oils:

	Fractions	Per cent of Fraction	Per cent of Straight Oil
210° C	9.7	25.0	2.4
235°	9.0	10.0	0.9
270°	12.3	10.0	1.2
315°	13.7	10.0	1.4
355°	15.0	15.0	2.3
	59.8		8.2

Total per cent paraffin in fractions below 355° C.	13.7%
Total per cent paraffin in fractions below 355° C. based on whole oil	8.2%

IV. SUMMARY.

1. Coke of good density and hardness may be made by mixtures of semi-coke and raw coal if both are finely divided and evenly mixed. A variation is noticeable in the quantity of such non-coking material which may be incorporated with different coals. For example, fresh coal from Vermilion County will carry such an addition of 100 per cent of its weight to advantage. Coals from Saline and Williamson Counties give coke of the highest density when mixed in the proportion of 50 per cent of their weight with semi-coke.

2. The coke resulting from the low temperature process has from 18 to 22 per cent of volatile matter remaining, but since it has been heated above 400° there should be none of the tar constituents remaining. The most convincing test on this point as also the best method of arriving at a conclusion as to its adaptability for such work was to try out the material in a suction gas producer. The results indicated that

no clogging effect whatever results, thus showing the absence of tar bodies. The physical operation of the producer as well as the grade of the gas produced was fully equal if not superior to the performance of the outfit when anthracite was used.

3. The semi-coke has such an amount of volatile matter remaining, together with the right degree of coherence as to make it especially well adapted to household use. It is clean to handle, free from dust, and burns without smoke or the formation of soot. Especially to be noted in this connection is its ability to retain a fire without undue attention as to drafts, etc.

4. The average specific gravity of the tar is 1.069. It is rich in low boiling distillate passing over at 210°. This product averages 18 per cent of the total. The pitch residue amounts to approximately 30 per cent and is remarkably free from precipitated carbon.

5. The adaptability of the tar for wood preservation processes seems to be indicated by the high percentage of tar acids. These constituents make up from 28 to 30 per cent of the crude material. The larger part, about 22 per cent is found in the second distillate (210°–325°), only about 7 per cent coming over below 210°.

6. Approximately 10 per cent of the crude tar is found to be low boiling distillate free from the tar acids and suitable for use in internal combustion engines.

7. Naphthalene is absent. The free carbon in the crude tar is less than 2 per cent and the residual product after the light distillate and heavy oils are removed would be classed as hard pitch.

8. A principal feature results from this study of these various substances, namely, that all three of the general divisions of coke, tar, and gas have specific properties of an especially valuable sort which would indicate that the process of coking at low temperatures could be established successfully on a commercial basis.

V. Review of Literature.

In the effort to solve the smoke problem which arises wherever bituminous coal is extensively used, numerous attempts have been made to modify the raw fuel in various ways in order to obtain a product which should be more or less free from smoke producing constituents. Among the first to make the attempt was Col. Scott-Moncrieff,* who proposed to subject coal to the coking process in the ordinary gas re-

*Jour. of Gas Lighting, 101, 823.

torts at the usual temperature until one-half of the volume of gas usually obtained was driven off. The charge was then drawn and quenched.

The scheme resulted in failure for very obvious reasons. On account of the porosity of coke it is a very poor heat conductor and so the interior of the charge received an insufficient amount of heat to drive off the tar and smoke producing substances while on the other hand the exterior was heated to such a degree that it became essentially hard gas-coke which ignited with difficulty and burned slowly. A mass consisting of a soft uncarbonized interior and a hard shell was the result, a type of fuel which possessed no good qualities and which gained no popularity. At the same time the manufacturer lost one-half of the gas and much of the ammonia that would be produced in ordinary practice.

*In 1907 a radical change in the method of heating was made by W. Parker and the product obtained was extensively advertised under the trade name of "Coalite." This was the coke made by the partial distillation of slack coal in vertical oblong cast iron boxes or stills about ten or twelve feet high and ten by forty-eight inches in cross section. Carbonization was carried on at temperatures near 450° C, yielding a coke having about 10 per cent of volatile matter and 80 per cent of fixed carbon.

The following table shows the composition of the gas obtained in the distillation.

TABLE 16.

COMPOSITION OF GAS OBTAINED IN COALITE MANUFACTURE.

H_2S	1.0	H_2	14.30
CO_2	3.45	CH_4	61.00
O_2	.72	N_2	9.28
Illum.	4.19	CO	6.06

Coalite has not proved to be the commercial success that its promoters hoped to make it, but experimental work is still being carried on with that end in view.

The Premier Tarless Fuels Company† of Battersea, England, have lately installed a plant for the production of smokeless fuel by low temperature distillation. The distinctive features are the use of annular retorts which allow the thickness of the charge to be reduced to 2½ inches and the coking time to be shortened proportionately, and

*Gas World, June 8, 1907. p. 715.
†Jour. of Gas Light & Water Supply. 122, 514.

the maintainance of a reduced pressure of 27 inches in the retorts. Temperatures of about 500° C are used and the charge is drawn at the end of four or five hours.

A sample yield from a Lancashire coal is given below.

TABLE 17.

YIELD OF PRODUCTS FROM VACUUM PROCESS.

Tarless fuel	78.0 per cent
Tar (per ton of coal)	20.19 gal.
Ammonium sulphate (per ton)	45 lb.
Approximate Composition of Fuel	
Fixed carbon	92.86
Volatile matter	3.86
Ash	3.28

This fuel is said to work well in the gas producer. Another sample with 8.26 per cent of volatile matter gives good results when used for domestic purposes, burning with a free flame, giving out intense heat and little smoke.

In considering the subject of tars and gases and their relationship to the matter of economy in coal carbonization no attempt will be made to review the great mass of literature relating to them, but merely to call attention to results which show causes for variation in the quality and yield, chief of which are range of distillation temperatures and differences in the sizes and shapes of the retorts.

The results obtained by Lewis P. Wright,* published twenty-five years ago, show the effect of increase in heat intensity in a striking manner. He does not state definitely the temperatures at which the different tars were produced but the following table compiled from his data indicates clearly that the gradations were marked.

TABLE 18.

RESULTS OF FOUR RUNS (2cwt. charges).

Sp. Gr. Tar	Duration of Distillation	Gas Yield per Ton of Coal, Cu. Ft.	Free Carbon in Tar, Per Cent
(1) 1.084	8 hrs.	6600	8.69
(2) 1.103	7 hrs.	7200	11.92
(3) 1.149	6 hrs.	8900	15.53
(4) 1.204	5 hrs.	11700	24.67

His analyses of the tars obtained show the characteristic increase in volatile constituents with rise in distillation temperature.

*Jour. Soc. Chem. Ind. 7, 59.

TABLE 19.

PERCENTAGE COMPOSITION BY WEIGHT OF TARS.

	No. 1	No. 2	No. 3	No. 4
Crude naptha	9.17	9.05	3.73	.99
Light oil	10.50	7.46	4.47	.57
Creosote oil	26.45	25.83	27.29	19.44
Anthracene oil	20.32	15.57	18.13	12.28
Pitch	28.89	36.80	41.80	64.08
Paraffin contents of crude naptha (by volume)	5.0	4.0	1.5	1.0

There is, likewise, a consistent fall in the percentages of the acid in the liquid fraction as the following table shows.

TABLE 20.

PERCENTAGE OF TAR ACIDS.

	In Crude Naptha	In Light Oil	In Creosote
No. 1	13	34	35
No. 2	9	35	29
No. 3	8	29	28
No. 4	6	22	20

Napthalene and anthracene become prominent in the heavier tars according to his investigations, the former appearing in considerable quantity in No. 4 and the latter being at its maximum in No. 3.

As proof that the tendency of increased temperature in the distillation of coal is to destroy, preferably, the phenol bearing light oils intermediate between the crude naptha and the creosote, he cites the case of a tar of specific gravity 1.33, distilled at high temperatures, which showed practically no light oils but which yielded solid napthalene immediately after the naptha had come over. Watson Smith, in an article on "Variation in the Products of the Destructive Distillation of Coals,"* confirms these results, by stating that tars which were produced at very high temperatures in Simon-Carves ovens and examined by him, showed a conspicuous lack of the middle oil fraction which contains the phenols and that the creosote and anthracene oils were semi-solid, the former being thick with napthalene.

He calls attention to a theory of Schulze† that the primary products of the dry distillation of coals are phenols. These phenols are

*Jour. Soc. Chem. Ind. 8, 952.

†Annalen, 227, 143.

then at the higher temperatures of the retorts split up so as to yield water and high boiling hydrocarbons, or finally, with more entire decomposition, into illuminating gas.

An interesting table showing the effect of change of temperature on the yield of gas and tar is given by V. B. Lewes.*

TABLE 21.

VARIATION OF GAS AND TAR YIELD WITH TEMPERATURE RANGE.

Temp. (C)	Gas yield per ton, cu. ft.	Tar gallons	Sp. gr. of Tar
900°	11 000	9	1.200
800°	10 000	12	1.170
700°	9 000	15	1.140
600°	7 750	18	1.115
500°	6 400	21	1.087
400°	5 000	23	1.060

Lewes points out that tars produced at temperatures between 400° C and 500° C contain relatively low percentages of aromatic substances and high percentages of the paraffin series which are adapted to use as motor fuels. The middle oils are free from napthalene and yield excellent enriching oils. The pitch having practically no free carbon, he says, forms an ideal electric insulating material.

Variations in the quality and composition of the gas are shown in the following table.

TABLE 22.

COMPOSITION OF GASES PRODUCED AT DIFFERENT TEMPERATURES.

	400°	500°	600°	700°	800°	900°
Hydrogen	21.2	28.3	33.8	41.6	48.2	54.5
Saturated hydrocarbons	60.1	56.2	30.7	45.0	39.1	34.2
Unsaturated hydrocarbons	6.3	5.8	5.0	4.4	3.8	3.5

The gas produced at the lowest temperatures quoted has a calorific value of 750 B.t.u. and measures 20 candle power.

Dr. H. W. Jayne, in a paper† before the Fifth International Congress of Applied Chemistry at Berlin in 1903, says in regard to coal tars:

*Jour. of Gas Light. 101, 823.

†The Coal Tar Industry in the U. S. Report of the Fifth International Congress of Applied Chemistry, Section IVa, Volume II, p. 721.

"The influence of the temperature in carbonizing is strikingly shown by the test of two tars, both from the same coal, and made in the same kind of ovens. One plant was producing gas as its main object. The tar from this source had a gravity of 1.21 and tested 17.5 per cent of free carbon; the light oil fraction was 2.2 per cent of a gravity 0.979, testing 23 per cent to 170 deg.; the pressed napthalene yield was 7.4 per cent. In the second tar, in which coke was the main object, evidently much lower heats were used, the tar having a gravity of 1.137, and testing 3.2 per cent of free carbon; the light oil amounted to 11.9 per cent, and had a gravity of .970, testing 28 per cent to 170 deg., or six times more crude naptha than in the first; the total tar acids were 12.48 per cent, while the pressed napthalene fell to 1.2 per cent." It is evident, he thinks, that in the first tar the light hydrocarbons and tar acids had been destroyed by the temperature employed, with formation of napthalene.

R. P. Perry* states that "Depending upon the coal used and more particularly upon the size and shape of retorts, the travel which the gases make over the hot surfaces, and the temperatures to which the gas is subjected, the coal tars vary within wider limits. In general with the vapors subjected to the high temperatures usually characteristic of gas works as compared with coke works, there is an increase in specific gravity and free carbon. For example the tar from many gas works will average about 1.24 specific gravity at 15.5°C. and about 25 per cent to 30 per cent free carbon by weight, whereas from the by-product coke ovens the specific gravity would average more nearly 1.19 and the free carbon would vary about 5 per cent to 18 per cent, the average being less than 10 per cent."

This so-called free carbon represents a finely divided inert material, largely carbon, which is the portion of tar insoluble in benzol and toluol. Perhaps a very small part is carried over mechanically in the coking process, but for the most part it is due to the cracking of the hydrocarbons by exposure to heat, and the higher percentage usually found in gas works tars is from this cause."

S. R. Church of the Barrett Manufacturing Company, in an interesting article on "Tar and Its By-Products,"† gives a table of results of analyses which were made in his laboratory, of the typical coke-oven tars produced in the United States. It is to be noted that the different

*R. P. Perry. Tar Distillation in the U. S. Eighth International Congress of Applied Chemistry. 10, 233.

†"Tar and Its By-Products," Gas Age, May 15, 1913.

gas retorts and ovens used vary in size and shape and that the former are, of course, heated to a much higher temperature than the latter.

TABLE 23.

ANALYSES OF TYPICAL TARS; DRY TAR.

	Gas Retort				Coke Oven			
	Horizontal		Inclined	Vertical	United Otto	Semet-Solvay	Koppers	Water gas Eastern
Specific gravity at 15.5° C.	1.266	1.293	1.238	1.153	1.207	1.188	1.186	1.083
Free carbon (insoluble in C_6H_6)	28.8	37.5	24.3		13.3	10.7	6.8	0.1
Specific viscosity (Engler at 100°C)	21.8	30	14.9	2.1	3.4	3	2.1	1.6
Oil to soft pitch 60°C. (Per cent by volume)	13.2		14.3	28.8	21.2	21.8	35.3	43.1
Pitch residue 60°C. mp (Per cent by volume)	86.8		85.7	71.2	78.8	78.2	64.7	56.9
Refractive indices at 60° C. (taken on oil)	1.5932		1.5807	1.5755	1.5987	1.6122	1.6139	1.5678
Sulphonation residue (Per cent taken in oil)	0.4		2.4	4.3				8
Tar acids (Per cent taken in oil)	14.		21.0	29.	12	4		

The figures given here are especially significant when compared with those of low temperature tars.

Vivian B. Lewes* in the series of articles mentioned earlier says of the tar produced in the manufacture of coalite, distilled at 400° to 500° C.: "The low-temperature tar is distinctive in its characteristics. It has a specific gravity of 1.075, is very liquid, and contains an abundance of light solvent oils, very low aromatic hydrocarbons, very little phenol but large quantities of cresol, no napthalene, and very little anthracene, while the free carbon is as a rule below two per cent."

The very low percentage of benzene in the light oils, is made up for by the presence of paraffins, such as hexane, heptane and octane, while there are also present considerable quantities of that curious group of hydrocarbons known as napthenes or hexahydro-benzenes, which play so important a part in Russian petroleum.

As before mentioned, carbolic acid occurs in small quantities, but its higher homologues, such as cresylic acid, etc., occur in much larger quantities than in coal tar, and there are also present quantities of polydydric phenols, or other esters of the type met with in coal tar which form resinous masses difficult to analyze. He states that coals rich in oxygen (10 to 11 per cent) and hydrogen (above 5 per

*The Carbonization of Coal. Lecture IV. Jour. Roy. Soc. Arts. 60, 216.

cent) and which, therefore, have large percentages of resinic bodies, on being carbonized at low temperatures yield tars rich in phenol and cresol. These results are confirmed by Bornstein. The pitch left as a residue amounts to about 40 per cent of the tar, and is of fine quality owing to the practical absence of free carbon. The ammonium sulphate amounted to only 12 lb. per ton of coal, the temperature being too low for large production.

The tar yield varies with the coal used and in most cases averages twenty gallons per ton of coal.

TABLE 24.

COMPOSITION OF TAR FROM COALITE.

Specific Gravity 1.073
Distillation on 2,274 cc. (0.5 gallon)

	Temp.	By volume on tar	Sp. gr.	Volume of hydrocarbons	Tar acids
Water		2.64			
Light Oil	170°	3.10	.844	3.10	
Carbolic Oil	170°–225°	13.72	.959	8.62	4.80
Creosote Oil	225°–240°	8.35	.988	4.64	3.10
Creosote Oil	240°–270°	8.35	.992	5.45	2.55
Anthracene Oil	270°–300°	8.80	1.029	6.60	1.76
Anthracene Oil	300°–320°	12.31	1.033	8.80	3.10
	Pitch by weight on volume			41.71%	
	Bases			1.32%	

	Light Oils Percentage distilling below	Calculated on Tar
100° C	15.6 by vol.	.55
120°	31.2	1.09
140°	54.7	1.91
170°	82.8	2.90
over 170° and loss	17.2	.20

Prevost Hubbard* has lately published a similar table of his own results obtained from the analyses of tars from twenty-six of the thirty-one by-product coke ovens operating in this country in 1910. His figures may be considered as showing authoritatively the character of the 67,000,000 gallons of tar produced from these sources in that year.

The specific gravities of the samples ranged from 1.133 to 1.214, the majority being lower than 1.200 and indicating low percentages of free carbon. The minimum percentage of free carbon was 2.73, the maximum 16.80, and the average for the 26 samples was 8.38. Eighteen samples contained less than 10 per cent of free carbon, and eight samples more than 10 per cent. About two-thirds of these products

*Coke-Oven Tars of the United States, Circular No. 97. Office of Public Roads, U. S. Dept. of Agriculture.

might, therefore, be considered as low-carbon tars and the other third, as medium carbon tars.

In accordance with the type of oven in which these products are made, there is a considerable variation in composition, even though temperatures differ but little. It seems probable, therefore, that high pitch and free carbon contents are not simple functions of temperature alone but that other factors complicate the problem.

TABLE 25.

COMPARISON OF TARS FROM VARIOUS TYPES OF OVENS.

Kind of Oven	Maximum Temperature of Retorts (C)	Per Cent Free Carbon	Per Cent Pitch Residue
Koppers	1100°–1444°	3.38	70
Semet-Solvay	1050°–1450°	6.74	63–79
United Otto	1220°–1660°	9.00	69–78
Otto Hoffman	1000°–1100°	12.16	60–78
Otto Hoffman and United Otto (mixed)	1000°–1200°	12.51	76
United Otto and Rothenberg (mixed)	1000°	17.17	76

Furthermore, the tars from different ovens of the same type show marked inconsistencies in many respects. For instance, twelve tars from as many different Semet-Solvay plants in which retort firing temperatures were in each case 1050°–1450° C, and maximum temperatures to which coal was brought, 950°–1150° C, show amounts of free carbon ranging from 4 per cent to 9 per cent; of pitch, from 63 per cent to 79 per cent; and of anthracene oils, from 5.5 per cent to 11 per cent.

Lunge,* the authority on coal tars, discusses only very briefly the effect of temperature range on the quality of tar. Among others, he quotes Behrens,† who found that the tar obtained in the distillation of coal in the ordinary fire-clay gas-retorts was much richer in benzene, tolene, and napthalene than that made from the same kind of coal in coke ovens operated at a lower temperature.

In considering and comparing the foregoing reports it should be borne in mind that as yet no standard or official methods for tar analysis and testing have been adopted by the industry as a whole. It is true, that while the manufacturers of special products such as creosote and road material, each in his own particular field has defined, more or less, his standards, the results obtained are not always comparable, and this is especially true when dealing with such complex hydrocar-

*Lunge, Coal Tars and Ammonia, 4th ed. 1909.

†Dingler's Polytech. Jour. 208, 362.

bons as coal tars. In spite of this difficulty, however, there is sufficient unanimity among the authorities to establish the fact fully confirmed by the worker in organic chemistry that rise of temperatures tend to produce polymerization with the formation of more complex substances of higher molecular weight, and that comparatively valueless products such as naphthalene and heavy pitch are produced in increasing quantities. In other words, the lighter and more valuable hydrocarbons are being destroyed in favor of the heavier ones which find little industrial use.

VITA

The writer received his elementary and secondary school training in the public schools of O'Brien County, Iowa. In 1908 he was graduated from the University of Iowa with the degree of Bachelor of Arts. From 1908 to 1910 he was instructor in Physics and Chemistry in the University Preparatory School of Oklahoma, leaving at the end of that period to accept a fellowship in Chemistry in the Engineering Experiment Station at the University of Illinois. He was granted the degree of Master of Science at Illinois in 1911. In the year 1913-1914 he was instructor in Chemistry at Vassar College and at the present time holds a similar position at the University of Illinois.

He has published with Professor S. W. Parr: "The Coking of Coal at Low Temperatures with a Preliminary Study of the By-Products," Bulletin No. 60, Engineering Experiment Station of the University of Illinois, 1912.

He is a member of Gamma Alpha, Phi Lambda Upsilon, Sigma Xi, and the American Chemical Society.